First Principle Static, Dynamic and Electronic Properties of Liquid Metal Alloys: A Case Study of Amalgams

A Synopsis
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1 Title

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2 Introduction

Solids, liquids and gases are classified as different states of matter [1] because each has a different way of organizing its atoms and molecules. Molecules in a solid are tightly packed, while molecules in a gas move freely. A liquid [2–4] is considered to be condenesed phase of matter. It has a density similar to solid phase, but has symmetry more like to a gas. Many properties of liquids e.g. specfic heat [3] are similar to that of solids at comparable temperatures, but they are generally much diificult to calculate than solid states or gaseous properties. For example at the melting point, the specfic heat for sodium (Na) at constant volume C_V is quite close to the specfic heat [3] of a monoatomic solid, $3Nk_B$. This is surprising in the case of an ideal fluid which cannot support transverse vibrational modes, which are responsible for specfic heat contribution. Mixture of atoms of two or more different liquid metals gives us liquid metal alloy. From a metallurgical point of view liquid alloys are very important because many solid binary alloys are formed initially by cooling from a liquid alloy. This is important from the point of view of understanding energetics of the formation of solid alloys also. An understanding of liquid alloys may also help to understand the stability of metallic glasses [5,6] which are metastable amorphous systems formed by rapidly quenching liquid alloys of favourable compostion. Liquid alloys also have geophysical and astrophysical significance. The interiors of the planets may be made up in part of a liquid mixture of metallic hydrogen and helium, white dwarf may have even more exotic, quasi-metallic components. Alloys with miscibility gap in the liquid state are especially interesting for advanced bearing materials. The extensive application of liquid alloys in various branches of science and engineering make their geochemical properties of more significance. There have been a large number of studies both theoretically and experimentally [7–9], wetting and other surface properties of alloys. The multicomponent alloys [10] represent new area of research.

3 Review of the Literature

The compound forming liquid alloys have been widely investigated and in particular much attention has been paid for thermodynamic, structural and electronic properties of Hg-based liquid binary alloys which show anomalous behaviour in their thermodynamic properties as a function of concentration [10–12]. Faber [13] was the first to study the compound formation in liquid metals and alloys. Later, Bhatia and his collaborators [14] gave compound forming model which describes satisfactorily the thermodynamic properties of these alloys. Also, conformal solution model of Bhatia and Hargrove [14–16] has been applied to study a number of liquid binary alloys sucessfully. Bhatia and Thornton [16] derived an important relationship of change in concentration on thermodynamic properties. It is a phenomenological approach to study the structure factors through the classical theory of thermodynamics. Lately [12, 17–19] there has been a lot of interest in liquid alloys showing tendencies for simultaneous formation of two compounds. Hoshino [17] explained successfully the entropy of mixing of the liquid NaSn alloy [20], obtained experimentally by Tamaki et al [21], by assuming the existance of two kinds of compounds. Also, the information about surface tension of metal alloy systems is essential for understanding and prediction of crystal growth or phase properties of nano-scale particles. Because of the crucial role of the wetting in soldering processes, knowledge of the surface tension of liquid alloys is of great importance.

Huijben et al [22] measured structure factors of NaCs alloys over the whole concentration range for large number of compostions. They employed X-ray and neutron diffration method and found the tendency of phase seperation in the liquids. Also, Albas's [23] neutron diffraction study indicates the ordering in the liquids. Copestake [24] calculated the radial distribution functions and partial structure factors of Li_4Pb at different tempertures. They modeled the interionic forces by pairwise potentials that are strongly repulsive at small separations and coulombic at large seperations. Watabe and Hasegawa [25] firstly discussed the partial structure factor of liquid metals, which is considered as a binary mixture of electrons and ions. Young [26] studied the structure of pure liquid metals and the liquid alloys based on hard-sphere model. Aschroft and Lekner [27]

derived the structure factor based on exact solution of Percus-Yevick equation [28] for one component hard sphere system. For a binary hard-sphere mixture, Ashcroft and Langreth [29] and Enderby and North [30] obtained the partial structure factors based on the exact solution of Percus-Yevick equation [28] by Lebowitz [31]. Hoshino [32] obtained the expression for partial and total structure factors for the m-component hard sphere system, based on Hiroike's [33] exact solution of Percus-Yevic equation [24].

The analysis of the liquid systems is complicated due to the presence of many-body forces acting between the atoms and ions [34–37]. The orbitals of conduction electrons in the metals were simple and smooth in the region between ion cores, but are complicated by a noble structure in the region of the cores [38]. The potential energy of conduction electrons was relatively weak. Besides, it was easy to calculate the potential energy of electrons outside the core but it was diificult or impossible to calculate the actual potential energy in the core region where the potential was strong and orbitals were not like plane waves. However, we can replace the actual potential energy in the core region by the pseudopotentials that give the same wave function outside the core region as the actual potential. In view of this, pseudopotential theory has enoromously contributed to the advances in the properties of pure liquid metals [39]. Metallic liquids and alloys have been extensively studied using the model pseudopotential theories. Pseudopotentials derived from first principles are either energy dependent or nonlocal and these features make the calculation of pseudopotentials more tedious. Model pseudopotentials also deal with the problem of transferability. Because sometimes with change of environment, change of parameters is also required. Recently, the construction of pseudopotentials has been shifted from modelling to ab-initio [40]. Ab-initio pseudopotentials are also free from transferability defect. Also ab-initio methods provide a lot of information about electronic, static and dynamic properties [41]. The ab-initio calculations on which these pseudopotentials are based are Hartree-Fock calculations. Norm conserving pseudopotential concept allows improved calculations of atomic systems. However the alloying effects were easily incorporated in a pseudopotential theory based on the expansion of conduction electron states in terms of orthogonalized plane waves [42]. There are various formalisms of pseudopo-

tentials to study the dynamics of liquid metals and alloys [41]. J. Hafner [49] have studied metallic liquids using the pseudopotential theories. Some of these pseudopotentials which are used to study the liquid metals are Hard-sphere model potential [26], Heine and Abarenkov pseudopotential [43], Ashcroft's empty core pseudopotential [44], Ab-initio pseudopotential.

The concept of model pseudopotentials have been the most popular method for the study of transport properties of liquid metals and their alloys was developed by Faber and Ziman [13]. Vora et al [45] used local pseudopotential to study resistivity of lead based alloys. Gajjar et al [46] combined hard sphere reference system and pseudopotential approach for explaining the structural information. Dalgic et al [47] used effective inter-ionic pair potentials to study the structure of liquid metal alloys. The basic approach used in all above investigations is Faber and Ziman approach [13]. In this approach it is assumed that conduction electrons as in the case of liquid metals form a free electron gas in disordered liquid metal alloys. These electrons while interacting with the irregularly placed ions having appropriate pseudopotential get scattered.

Numerous attempts [49,50] have been made for the study of structure and dynamics of liquid metals and liquid alloys at their respective melting temperatures. Molecular dynamics is a recent approach to study the atomic motions in these alloys and metals. At the heart of molecular dynamics scheme is the question of how to approximate the interatomic interactions. Until 1980s, the structure of liquid was studied by integral-equation theories [48] and computer simulations such as molecular-dynamics (MD) and Monte Carlo (MC) simulations [51]. Interatomic potential was the input to carry out these simulations and standard method to obtain interatomic potential of liquid metals was pseudopotential perturbation theory [52]. Although this theory was successfully applied to simple liquid alkali metals, there are some limitations to its validity (e.g. the electron-ion pseudopotential must be weak, though this is not always the case). A breakthrough in the study of liquid metals was the new method proposed by Car and Parrinello [53] in 1985. It is a unified method of the molecular dynamics simulation for ionic dynamics and of the density functional theory (DFT) for electronic states and enables us to obtain simultaneously both the ionic arrangment and electronic

states at the same time. In this method interatomic potential need not be given as input, since the force acting on each atom is given within the framework of this method. This new method is called " ab-initio molecular dynamics simulation method." This method extended the applicabilty of DFT to non-periodic systems such as liquid metals and semiconductors, various surface systems, nanomaterials. There are many advantages of ab-initio molecular dynamics calculations such as information about density of state, ability to study reactions that involved breakage or formation of covalent bonds and structure of liquid metals.

In ab-inito molecular dynamics simulations, the electronic structure and total energy is evaluated using the density functional theory (DFT) and the corresponding forces are used to move the ions according to classical molecular dynamics. Using this approach it is possible to calculate both the atomic and electronic structure consistently and to study how changes in one are correlated with changes in other. The reason for this development are evident: LDA offers a reasonable compromise between accuracy and efficiency in treating electronic many body effects, is completely parameter free and with the enomorous increase in computer power complex calculations are now feasible. In recent years, the thermodynamic and transport properties of a number of liquid metals and alloys have been studied by this method [54–57]. Results from ab-initio molecular dynamics simulations are found to be in good agreement with experiments.

K. Hoshino [58] studied structure of liquid metals by ab-initio molecular dynamics simulations. In this paper it is emphasized that by ab-initio molecular dynamics simulations, electronic states as well as structure of liquid metals can be obtained at the same time. Recently, the spectra of longitudnal and transverse coolective excitations in liquid binary metallic alloys are studied using generalized collective modes approach to analyze the concentration dependence of dispersion of acoustic and optic branches in a wide region of wavenumbers [59]. An increasing number of powerful codes are able to perform ab-initio molecular dynamics simulations today such as ABINIT [60] , CASTEP [61], FHI98md [62], SIESTA [63] and VASP [64].

4 Basic Formulae and Approximations

Let the binary solution contain free atoms of A, free atoms of B and a chemical compound or pseudo molecule $A_\mu B_\nu$. Accordingly, we presume that μ atoms of A and ν atoms of B are energetically favoured to form chemical complex $\mu A + \nu B \rightleftharpoons A_\mu B_\nu$. Thus, we have a solution of n_1 atoms of A, n_2 atoms of B and n_3 atoms of complex AB which are subject to atomic concentration c_A=C for the A atom and c_B=1-C for the B atom with C_1+C_2=1. It is assumed that the chemical complexes of AB exist in molten phase. From the conservation of atoms, one has

$$n_1 = C - \mu n_3 \qquad n_2 = 1 - C - \nu n_3$$
$$n = n_1 + n_2 + n_3 \qquad n = 1 - (\mu + \nu) n_3$$

4.1 Free Energy of Mixing

The free energy of mixing (G_M) of the binary alloy can be expressed as

$$G_M = -n_3 g + \Delta G \tag{1}$$

where g is the formation energy of compound and the first term $-n_3 g$ represents the lowering of free energy of mixing due to formation of compound in the alloy, while ΔG represents the free energy of mixing of ternary mixture of A, B and $A_\mu B_\nu$ ($\mu = 1, \nu = 1$) for fixed amount of respective atoms n_1, n_2, n_3.

$$\begin{aligned} G_M &= -n_3 g + RT \sum_{i=1}^{3} n_i (ln(n_i) - ln(n)) \\ &+ \sum_{i<j} \sum \frac{n_i n_j}{n} W_{ij} \end{aligned} \tag{2}$$

where R is gas constant. W_{ij}(i,j=1,2,3) are the interaction energies through which the left-over A atoms, B atoms and $A_\mu B_\nu$ compound interact with one other. By definition, W_{ij}, the interaction energies are independent of the concentration but may depend on the temperature and pressure. The equilibrium values of n_3 are obtained via the minima condition for G_M

$$\left(\frac{\partial G_M}{\partial n_3} \right)_{T,P,C} = 0 \tag{3}$$

which gives rate equation or mass-action equation

$$\frac{n_1^{\mu} n_2^{\nu}}{n_3 n^{\mu+\nu-1}} = k e^{Y} \tag{4}$$

Where k=$e^{-\frac{g}{RT}}$ **and**

$$\begin{aligned} Y &= \frac{W_{12}}{RT}\left((\mu+\nu-1)\frac{n_1 n_2}{n^2} - \mu\left(\frac{n_2}{n}\right) - \nu\left(\frac{n_1}{n}\right)\right) \\ &+ \frac{W_{13}}{RT}\left((\mu+\nu-1)\frac{n_1 n_3}{n^2} - \mu\left(\frac{n_3}{n}\right) - \left(\frac{n_1}{n}\right)\right) \\ &+ \frac{W_{23}}{RT}\left((\mu+\nu-1)\frac{n_2 n_3}{n^2} - \nu\left(\frac{n_3}{n}\right) - \left(\frac{n_2}{n}\right)\right) \end{aligned} \tag{5}$$

It is obvious that to compute n_3 **or** G_M **we must have the knowledge of g and** W_{ij}**. The formation energy of compound g and mutal interaction energies between three constituents of the alloy** W_{ij}**s can be determined following the method suggested by Bhatia and Hargrove [15]. Interaction energies [65] between two species (**W_{ij}**) inevitably play an important role in the formation of compounds. If these interaction energies are concentration dependent, then certainly the thermodynamic properties are likely to change and better agreement with experiments is expected. It may, however, be noted that, once the energy parameters are selected, these remain the same for all other investigations such as concentration fluctuations, activity, heat of mixing and entropy of mixing.**

Once the expression for G_M **is there, other thermodynamic functions, (e.g. Heat of mixing** H_M **and Entropy of mixing** S_M**), which are related to** G_M **through various thermodynamic relations can be obtained. The free energy of mixing** G_M**(equation(4)) can be used to obtain an expression for the activity** a_A **of atom A as follows:**

$$\begin{aligned} RT\ln a_A &= RT\ln\left(\frac{n_1}{n}\right) + \left(\frac{n_2}{n}\right)W_{12} + \left(\frac{n_3}{n}\right)W_{13} \\ &- \frac{1}{n^2}\sum_{i<j}\sum n_i n_j W_{ij} \end{aligned} \tag{6}$$

with the same values of n_i**(i=1, 2, 3) and energy parameters, equation(8) can be used to compute activity as a function of concentration.**

The heat of mixing can be obtained using equation (2) for G_M **in the relation**

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{T,P} \tag{7}$$

and hence the entropy of mixing

$$S_M = \frac{(H_M - G_M)}{T} \tag{8}$$

Later equations (7) and (8) are used to ascertain the variation in energy parameters with temperature [66].

4.2 Concentration fluctuations at long-wavelength limit and Short range order parameter

One of the most important quantities in the study of liquid alloys is the concentration-concentration correlation function Scc(o) [16]. S_{cc}**(o) indicates the kind of local order and level of complex activities present in the alloy.** S_{cc}**(o) in the long wavelength limit is obtained by differentiating equation(2) with respect to concentration C.**

$$\begin{aligned} S_{cc}(o) &= \sum_{i=1}^{3} \frac{(n_i^{'})^2}{n_i} - \frac{(n^{'})^2}{n} \\ &+ \frac{2n}{RT} \sum_{i<j} \sum \left(\frac{n_i}{n}\right)^{'} \left(\frac{n_j}{n}\right)^{'} W_{ij} \end{aligned} \tag{9}$$

The deviation of S_{cc}**(o) from ideal values (**S_{cc}^{id}**(o)=C(1-C)) can be used to visualise the nature of atomic order in the alloys. A measure of tendency to compound formation or phase separation in a molten alloy is given by Warren-Cowley short range order parameter** α_1 **[67, 68]. For nearest neighbour sites,** α_1 **can be defined as** $\alpha_1 = 1 - [P_{AB}/1 - C]$ **whereas** P_{AB} **is conditional probability of finding a B atom nearest to atom A. In terms of unlike atoms this equation can be expressed as**

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1}, \qquad S = \frac{S_{cc}(o)}{S_{cc}^{id}(o)} \tag{10}$$

where Z is coordination number.

4.3 Diffusion

The mixing behaviour of two molten metals forming binary alloys can be analysed at the microscopic scale in terms of diffusion. The formalism that relates diffusion and Scc(o) combines the Darken thermodynamic equation for diffusion with the basic thermodynamic equations

in the form [69]

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(o)}{S_{cc}(o)} = \frac{C(1-C)}{S_{cc}(o)} \tag{11}$$

where D_M is the mutal diffusivity of the alloy and D_{id} is the intrinsic diffusivity for an ideal mixture of liquid alloy components which can be obtained from D_{id} = C D_B + (1 - C) D_A. The highest peak of D_M/D_{id} vs. concentration suggests the presence of maximum chemical order in molten alloy system as well as the compostion of the most probable associates to be formed in liquid. In case of ideal mixing $D_M/D_{id} \rightarrow 1$ and for segregation $D_M/D_{id}<1$ i.e. $D_M<D_{id}$.

4.4 Surface tension

Using Butler's equation [70, 71], surface tension can be derived from the surface tension of the pure components. Recently, a model of surface tension of binary alloys with compound formation was proposed [72]. Prasad et.al. [73] gave the expression for surface tension of binary alloys in terms of activity coefficient of alloy components as [74]

$$\begin{aligned} \xi &= \xi_A + \frac{KT}{a} \ln \left(\frac{C_A^s}{C_A} \right) \\ &- \frac{KT}{a} \ln \gamma_A + [p(C_B^s)^2 + q(C_B)^2] \frac{W}{a} \end{aligned} \tag{12}$$

or

$$\begin{aligned} \xi &= \xi_B + \frac{KT}{a} \ln \left(\frac{C_B^s}{C_B} \right) \\ &- \frac{KT}{a} \ln \gamma_B + [p(C_A^s)^2 + q(C_A)^2] \frac{W}{a} \end{aligned} \tag{13}$$

where ξ_A and ξ_B are surface tension of pure components A and B respectively. C_i and C_i^s are bulk and surface concentration of alloy components respectively. γ_A and γ_B are bulk activity coefficient [75, 76] of alloy components and W is the interchange energy [73]. Here p and q are surface coordination fractions.The surface coordination fractions p and q are fractions of total number of nearest neighbours within the layer, in which it lies and that in the adjoining layer respectively, so that $p + 2q = 1$. For closed packed structures one has p=0.5 and q=0.25. Also

$$\gamma_A = \left(\frac{\beta - 1 + 2C}{c(1+\beta)} \right)^{(\frac{1}{2})Z} \qquad , \gamma_B = \left(\frac{\beta + 1 - 2C}{(1-c)(1+\beta)} \right)^{(\frac{1}{2})Z} \tag{14}$$

with $\beta = [1 + 4C(1-C)(\eta^2 - 1)]^{\frac{1}{2}}$. However, for a simple regular alloy η is given by η=exp $(\frac{w}{ZKT})$ where c is concentration of A species and w is the order energy. The surface tension of pure components of alloy is given by

$$\xi_i = \xi_{im} + (T - T_M)\frac{\partial \xi_i}{\partial T} \tag{15}$$

where ξ_{im} are the surface tension of alloy components at their melting temperature T_M and T is working temperature in kelvin. The atomic surface area A_i for each atomic species of different alloy systems are calculated using the result [77] $a_i = 1.102\left(\frac{\vartheta_i}{N}\right)^{\frac{2}{3}}$ and the mean surface area a is then given as $a = \Sigma c_i a_i$ where N is the Avogadro's number and c_i are concentrations of the alloy components, ϑ_i are volume of alloy components. For surface concentration the ideal solution model gives

$$C_A^s = \left(\frac{C_A}{C_A + \frac{C_B}{S_o}}\right), \qquad C_B^s = \left(\frac{C_B}{C_B + C_A S_o}\right) \tag{16}$$

where S_o is surface segregation factor [72]. This factor is the ratio between energy gained by surface segregation and the thermal energy. The idea is to modify this factor by taking into account the fact that some of surface active atoms may be bound in clusters. For these, the energy gain by surface segregation must be reduced by the energy required to break a cluster of A_nB_m. Consequently, we replace S_o [79] by S_{AB}

$$S_{AB} = \exp\left(\frac{A(\gamma_B - \gamma_A) - f(n+m)C_A^n C_B^m}{RT}\right) \tag{17}$$

where f represents the molar binding energy of cluster [73] and A=A_i is the surface area.

4.5 Hard-sphere diameters

One of the fundamental properties of liquid is that it possesses short range order as compared to long range order in crystalline solids. To investigate the short-range order in liquids, one of the significant function is the structure factor and partial structure factors. These structure factors along with pair potentials further provide inputs to understand structural, thermodynamic and electronic properties of liquids [80]. To calculate partial structure factors, hard sphere diameters are required. In order to calculate hard sphere diameters

inter-ionic pair potentials are calculated by generalizing Harrison's [52] approach of pairwise potential between the metallic ions. The pair potential has familiar form of the screened Coulomb potential given by:

$$V_{ij} = \frac{Z_i^* Z_j^*}{R}\left(1 - \frac{2}{\pi}\int_0^\infty F_{ij}^N(q)\frac{\sin(qR)}{q}dq\right) \tag{18}$$

where in equation (18) $Z_i^* Z_j^*$ [81,82] are effective valencies and $F_{ij}^N(q)$ is a normalized energy wave number dependent characteristic. In many cases especially for non-local pseudopotentials valence Z is replaced by effective valence Z^*. When a non local pseudopotential is used, the calculation of $F^N(q)$ and Z^* requires the self consistent solution of a system of coupled non-linear equations [81]. The effective valence charges Z_i^* and Z_j^* are given in the form $Z_i^* Z_j^* = Z_i Z_j - \overline{Z_i}\ \overline{Z_j}$. where Z is the true valence and $\overline{Z}$ is the depletion hole charge that originates from orthogonality condition between valence and core electron wave functions. $F_{ij}^N(q)$ is given by:

$$F_{ij}^N(q) = -\left(\frac{q^2\upsilon}{2\pi Z_i Z_j}\right)F_{ij}(q) \tag{19}$$

where in the general case F_{ij}(q) is given by:

$$F_{ij}(q) = -\left(\frac{q^2\upsilon}{8\pi}\right)\left(w_i(q)w_j(q)\frac{\epsilon^*(q)-1}{\epsilon^*(q)}\frac{1}{1-G(q)}\right) \tag{20}$$

Here quantities $w_i(q), w_j(q)$ are fourier transforms of self consistent bare ion (unscreened) atomic pseudopotentials for metallic components of an alloy. G(q) is the exchange-correlation functional by Vashishta and Singwi [83]. ϵ^*(q) is modified Hartree dielectric function. Here $\upsilon = \upsilon_{ideal} = C_1\upsilon_1 + C_2\upsilon_2$ where C_1 and C_2 are the concentration of first and second component respectively and υ_1 and υ_2 are the atomic volume of pure elements. Once the pair potential is calculated then hard sphere diameters can be determined by minimising the interionic pair potential

$$V_{ij} = V_{min} + \frac{3}{2}K_B T \tag{21}$$

where $\frac{3}{2}K_B T$ is the mean kinetic energy and V_{min} is the first minimum of the interionic pair potential given by equation (3).

4.6 Partial structure factors

In the binary liquid with the formation of one compound, there are $\frac{3(3+1)}{2} = 6$ partial structure factors due to symmetric matrix i.e. $S_{ij}(k) = S_{ji}(k)$. To calculate the partial structure factors for a ternary mixture, the three component hard sphere mixture matrix is given by [32]:

$$S(k) = \begin{vmatrix} S_{11}(k) & S_{12}(k) & S_{13}(k) \\ S_{21}(k) & S_{22}(k) & S_{23}(k) \\ S_{31}(k) & S_{32}(k) & S_{33}(k) \end{vmatrix}.$$

$$= \begin{vmatrix} 1 - n_1 c_{11}(k) & -\sqrt{n_1 n_2} c_{12}(k) & -\sqrt{n_1 n_3} c_{13}(k) \\ -\sqrt{n_2 n_1} c_{21}(k) & 1 - n_2 c_{22}(k) & -\sqrt{n_2 n_3} c_{23}(k) \\ -\sqrt{n_3 n_1} c_{31}(k) & -\sqrt{n_3 n_2} c_{32}(k) & 1 - n_3 c_{33}(k) \end{vmatrix}^{-1}.$$

where c_{ij} are the correlation functions. These partial structure factors provide the input for calculating transport properties of liquid metal alloys.

4.7 Electrical Resistivity

Using the modified Faber Ziman approach [13], the electrical resistivity of a complex forming liquid alloy can be written as $R = R_1 + R_2$. Here R_1 represents the contribution to resistivity due to the scattering from bare A and B ions whereas R_2 represents the scattering contribution due to complex and can be expressed as:

$$R_1 = \frac{3\pi}{\hbar^2 e^2} \frac{4\upsilon}{V_F^2} \int_0^1 [x_1 w_1^2(q) S_{11}(q) + x_2 w_2^2(q) S_{22}(q) + 2\sqrt{x_1 x_2} w_1(q) w_2(q) S_{12}(q)](q/2k_F)^3 d(q/2k_F) \quad (22)$$

$$R_2 = \frac{3\pi}{\hbar^2 e^2} \frac{4\upsilon}{V_F^2} \int_0^1 [x_3 w_3^2(q) S_{33}(q) + 2\sqrt{x_2 x_3} w_2(q) w_3(q) S_{32}(q) + 2\sqrt{x_1 x_3} w_1(q) w_3(q) S_{31}(q)](q/2k_F)^3 d(q/2k_F) \quad (23)$$

Here $V_F = (\hbar k_F/m)$ is the Fermi velocity and $k_F = (3\pi^2 Z_s/\upsilon)^{1/3}$ is the Fermi wave vector. Z_s is the mean number of valence electrons per atom and is given by $Z_s = [C_1 Z_1 + C_2 Z_2] - 2n_3$. In equations (22) and (23) x_1, x_2, x_3 are fractions of concentration of the elements and the complex in an alloy. $w_1(q), w_2(q), w_3(q)$ are the respective non-local screened pseudopotentials.

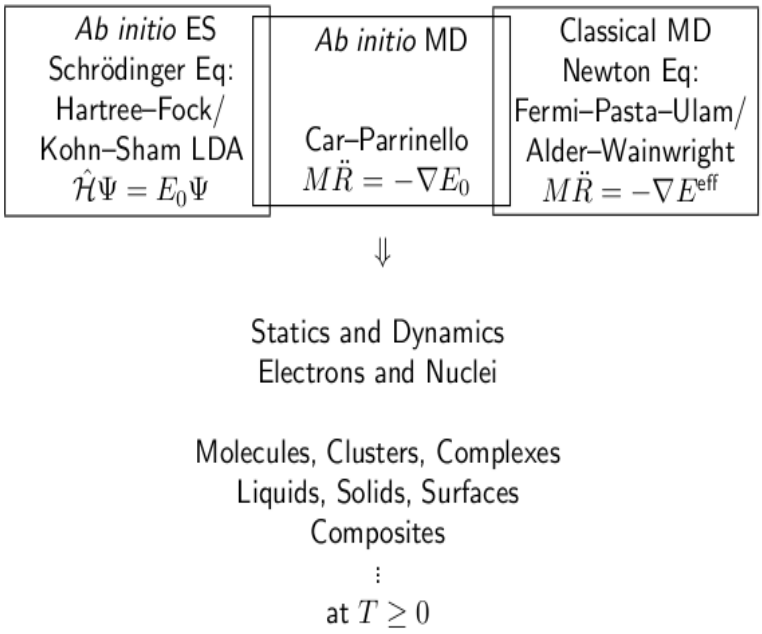

Figure 1: Ab-initio molecular dynamics unifies approximate ab-initio electronic structure theory (i. e. solving Schrodinger's wave equation, Hartree-Fock theory or the local density approximation within Kohn-Sham theory) and classical molecular dynamics (i. e. solving Newton's equation of motion numerically for a given interaction potential as reported by Fermi, Pasta, Ulam and Tsingou for a one-dimensional anhormanic chain model of solids [84] and Alder and Wainwright for the three-dimensional hard-sphere model of fluids [85])

4.8 Ab-initio Study of Density Functional Theory

As stated in the review of literature density functional theory (DFT) is an extremely successful approach to compute electronic properties of matter. Density functional theory (DFT) is a quantum mechanical modeling method used in physics to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules. The basic idea underlying every ab-initio molecular dynamics method is to compute the forces acting on the nuclei from electronic structure calculations see Fig. 1 for a simplifying scheme.

4.8.1 Structure and Thermodynamic Properties [86]

Molecular Dynamics simulations generate successive configurations of the system. The partial pair distribution $g_{ij}(r)$ can consequently be computed from positions of the atoms in a simulation box. These functions contain information about both topological and chemical order. These features are displayed by Bhatia-Thornton's partial structure factors [16]

$$\begin{aligned} S_{nn}(q) &= C_1 S_{11}(q) + C_2 S_{22}(q) + 2\sqrt{C_1 C_2} S_{12}(q), \\ S_{nc}(q) &= C_1 C_2 (S_{11}(q) - S_{22}(q) + \frac{C_2 - C_1}{\sqrt{C_1 C_2}} S_{12}(q)), \\ S_{cc}(q) &= C_1 C_2 [C_2 S_{11}(q) + C_1 S_{22}(q) - 2\sqrt{C_1 C_2} S_{12}(q)], \end{aligned} \tag{24}$$

where C_i is the concentration of the ith species. The first term measures the correlation local densities of atoms, second term measures the coross correlation between atomic density and concentration and third one mesures the correlation between local composition.

In the above formulas, Ashcroft-Langreth structure factors [29] that are related to the pair distribution functions, $g_{ij}(r)$ are given by

$$S_{ij} = \delta_{ij} + \sqrt{C_i C_j} \int_0^\infty [g_{ij}(r) - 1] \frac{\sin qr}{qr} 4\pi^2 dr \tag{25}$$

From the knowledge of thses $S_{ij}(q)$, total structure factor S(q) can be calculated to make comparison with x-ray or neutron diffusion experiments. Thus

$$S(q) = \frac{C_1 f_1^2 S_{11}(q) + 2\sqrt{C_1 C_2} f_1 f_2 S_{12}(q) + C_2 f_2^2 S_{22}(q)}{C_1 f_1^2 + C_2 f_2^2} \tag{26}$$

where f_i correspond to x-ray or neutron form factor of an atom of type i.

Some thermodynamic properties of the system are related to these structure factors as follows [86]

$$\begin{aligned} S_{cc}(o) &= N k_B T / (\frac{\partial^2 G}{\partial C^2})_{T,P,N} \\ S_{nn}(o) &= \frac{N}{V} k_B T \chi_T + \delta^2 S_{cc}(o) \\ S_{nc}(o) &= -\delta S_{cc}(o) \end{aligned} \tag{27}$$

In these equations, G is the Gibbs free energy, χ_T is the isothermal compressibility and δ is a dilatation factor defind as $\delta = N(v_1 - v_2)/V$, with v_i denoting partial molar volume of ith species.

4.8.2 Diffusion Properties

As in pure liquid, atoms of mixture diffuse into the matter.. This corresponds to self diffusion and is measured by self diffusion coefficients. In a mixture, however their is one cofficient for each chemical species which can be computed from the corresponding velocity autocorrelation fuction (VACF) as

$$D_i = \frac{1}{6}\int_{-\infty}^{+\infty} \psi_i(t)dt$$

$$\psi_i(t) = \frac{1}{N_i}\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau}\sum_{i=1}^{N_i} v_a^{(i)}(t_o)v_a^{(i)}(t_o+t)dt_o \tag{28}$$

There is also an additional phenomena in a mixture called interdiffusion (ability of both species to mix). Inter-diifusion coefficient is given by (e.g. for the case of species i and j)

$$D_{i/j} = \frac{C_1C_2}{S_{cc}(o)}\int_0^{\infty} V_D(t)dt \tag{29}$$

where

$$V_D(t) = \frac{1}{3NC_1C_2}\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} v_d(t_o)v_d(t_o+t)dt_o \tag{30}$$

is the autocorrelation function of the microscopic diffusion velocity

$$v_d(t) = C_2\sum_{i=1}^{N_1} v_i^{(1)}(t) - C_1\sum_{j=1}^{N_2} v_j^{(2)}(t) \tag{31}$$

Since mesurement and computation of interdiffusion properties are difficult, some useful approximations have been proposed among which Darken [87] model that gives the case where correlation between velocities of particles of different species can be neglected. So inter diffusion cofficient can be written as

$$D_{Dark} = \frac{C_1C_2}{S_{cc}(o)}(C_2D_1 + C_1D_2) \tag{32}$$

In case of ideal mixture, since $S_{cc}(o) = C_1C_2$, inter diffusion coefficient can be written as $D_{id} = C_2D_1 + C_1D_2$

c

5 Computational Method

Ab initio is a Latin term meaning "from the beginning". A calculation is said to be ab initio or from first principles if it relies on basic and established laws of nature without additional assumptions or special models. Ab-initio calculations used in the current work proposed to be described in two steps below.

5.1 Using Pseudopotential

As mentioned earlier in the review part the replacement of chemically inactive electrons by pseudopotentials is a comman method used in many kinds of electronic structure calculations. Different fields (LCAO methods, plane wave-based methods, quantum Monte Carlo methods) have developed their own flavor of such potentials. The norm-conserving pseudopotential approach of plane wave calculations provides an effective and reliable means for performing calculations on complex molecular, liquid and solid-state systems [44, 88]. In this approach only chemically active valence electrons are dealt explicitly. The inert core electrons are eliminated within the frozen -core approximation. They are considered as rigid non-polarizable ion cores with the nuclei. All electrostatic and quantum-mechanical interactions of the valence electrons with the core, such as the nuclear Coulomb attraction screened by the core electrons, Pauli repulsion and exchange and correlation between core and valence electrons, are accounted for by angular momentum (non-local) pseudopotentials. These reproduce the true potential and valence orbitals outside a chosen core region but remains much weaker and smoother inside. The valence electron are then described by smoother pseudo orbitals which play the same role as the true orbials, but avoid the nodal structure near the nuceli that keeps the core and valence states orthogonal in an all electron framework. The Pauli repulsion largely cancels the attractive parts of the true potential in the core region and is bulit into rather weak pseudopotential.

Practically, pseudopotentials should be additive and transferable. Additivity can most easily be achieved by building pseudopotentials for atoms in reference states. Tranferability means that one and the same pseudopotential should be adequate for an atom in all possible chemical environments. This is especially important when a change of the environment is expected during a simulation e.g. in chemical reactions of phase transitions. Ab-initio pseudopotentials are free from these defect. Moreover, ab-initio methods provide a lot of information about electronic, static and dynamic properties [41] such as free energy of mixing, diffusion, surface tension, hard sphere diameter, electrical resistivity etc., which enables us to have comparison with experimental results. Norm conserving pseudopotential concept allows improved calculations of atomic systems.

5.2 Using Density Functional Theory Calculation (DFT)

Density functional theory (DFT) is a theory of correlated many-body systems. DFT is a ground state theory in which emphasis is on charge density as the revlevant physical quantity. Density functional theory has proved to be quite successful in describing structural and electronic properties in a large class of materials which have range from atoms and molecules to complex extended systems. Density functional theory is computationally very simple and so DFT has become a comman tool in first principles calculations and describing the properties of molecular and condensed matter systems. At the heart of density functional theory have been three key results: (i) Hohenberg Kohn theorem [90], (ii) Kohn Sham equations, (iii) Local density approximation [91]. The remarkable successes of approximate local density (LDA) [92, 93] and generalised gradient approximation (GGA) [94] functionals within Kohn Sham approach have lead to widespread interest in density functional theory as the most promising approach for accurate, practical methods in the theory of materials.

Molecular dynamics simulations compute the motions of individual molecules in models of solids, liquids and gases. The key idea here is motion, which describe how postions, velocities and orientations change with time. In effect, molecular dynamics constitutes a motion picture that follows molecules as they move to and fro, twisting,

turning, colliding with one another. The ab-initio molecular dynamic calculations based on DFT [95] are different from the conventional DFT approach as in earlier approach Kohn-Sham energy functional for a given ionic configuration is minimized by some optimization method [96, 97]. The emerging of Car-Parrinello molecular dynamics (CPMD) [53] originates from the limitations suffered by both DFT and classical MD, which effectively restricted their application to the realistic simulation of condenesed matter at finite temperature to specific cases. Pure DFT was mainly applicable to the electronic structures of ordered and homogenous systems. By using DFT to calculate the potential of atoms and letting such potential evolve at each step of the simulation, CPMD allowed a much wider range of disordered and realistic systems to be studied. The main obstacle that prevents the use of potential energy surfaces derived from DFT in MD is high cost of quantum mechanical calculation. And this cost exist until the formulation of Car-Parrinello [53] approach come out.

Car-Parrinello [53] approach proposed to be (used in our calculations) is an extended Lagrangian formulation, in which both atomic and electronic degree of freedom act as dynamic variables. In it the electronic degrees of freedom ψ_i are minimized at the beginning, and then evolve together with the atomic degrees of freedom [98]. In CPMD the electrons follow the atomic motion adiabatically inspite of mass seperation between the electrons and ions. In this approach, the first principle molecular dynamics trajectory is generated without the need for re-minimization of the electron wavefunction at each time step and thus decreases the effort for the study of various systems. The remaining task is to seperate the atomic and electronic motion such that the fast electronic subsystem stay cold for long times but still follows the slow atomic motion adiabatically which is controlled by the ficitious mass parameter μ. Simulaneously, the nuclei must be kept at a much higher temperature. This can be achieved in non-linear classical dynamics via decoupling of the two subsystems (fast electrons and slow ions) and adiabatic time evolution.

In the current work it is proposed to use fully self consistent implementation of DFT called SIESTA (Spanish Intiative for Electronic Simulations with Thousands of Atoms) [99–101]. It is based on linear combination of atomic orbitals (LCAO) basis set with O(N) scaling. It provides fast calculations using small basis sets and very accurate

calculations with multiple-zeta and polarized basis sets depending upon the accuracy required and available computional power. Since this method is based upon localized orbitals, therefore, it is suited to describe systems with arbitrary dimensionality means from molecules or clusters to two dimensional surfaces to three dimensional crystals. We propose to use ab-inito molecular dynamics as a tool for studying liquid metals and liquid metal alloys [103].

6 Motivation and Objective

The outstanding properties of binary liquid alloys with strong non-ideal mixing behaviour have been of long standing interest in the past decade and are useful in diversified fields. The study of liquid alloys helps us to understand the interior of earth, which is considered as mixture of iron and nickel, and other planets which may be made up in parts of a liquid mixture of the metallic hydrogen and metallic helium. Alloys with miscibility gap in the liquid state are especially interesting for advanced bearing materials. Among the most important types of liquid alloys, which have interested many worker's because of their anomalous properties, are liquid amalgams. The alloying behaviour of liquid binary amalgams is of great significance, their thermodynamic properties show anomalous behaviour as function of concentration [104]. Earlier studies of thermodynamic and transport properties based their understanding (of these systems) through model pseudopotentials with a requirement of parameter fitting for energy. However, lately generation of ab-initio pseudopotentials [105] have started contributing significantlly in studying these properties. The binary liquid alloy have been found to exhibit anomalous thermodynamic, structural and transport properties [106] at the stoichiometric compostion. Also, with the emergence of Density Functional Theory (DFT) which has achieved remarkable success in looking at materials in bulk, surfaces and low dimensions, ab-initio molecular dynamics is being intensively used as a tool for studying liquid metals and liquid metal alloys [102, 103, 107]. Keeping this in mind, various thermodynamic, surface and transport properties of HgPb and HgIn alloys are proposed to be studied as given below:

- We have proposed to study the properties of compound forming

of liquid amalgam (of Pb and In) using Ab-inito pseudopotentials. The thermodynamic properties of binary liquid alloys show anomalous behaviour as a function of concentration. Keeping this in mind we have proposed to study the free energy of mixing (G_M) and interaction energies (Wij) of binary liquid alloys. We have proposed to study the properties of liquid amalgam (of Pb and In) alloy with one compound formation. The system in that case is considered as ternary mixture consisting of A atoms, B atoms, $A_\mu B_\nu$ compound.

- **The study of diffusion and surface properties, the statistical formulation of Prasad et al [73] based on concept of layered strucutre near the interface will be used.**

- **We propose to study the partial structure factors of binary liquid alloy. In order to determine the partial structure factors the hard sphere diameters σ_{ij} are determined by minimizing the interionic pair potentials V_{ij}. Here we have proposed to find the pair potential using Ab-initio pseudopotentials [105,108,109] instead of model pseudopotentials.**

- **The electronic properties like electrical resistivity will also be determined by ab-initio pseudopotentials. In earlier work only model pseudopotential for calculation of electrical resistivity of Hg-amalgam (of Pb and In) have been used.**

- **We also propose to study ab-initio molecular dynamics of mercury amalgams (of Pb and In) using SIESTA code [99–101]. Structural and thermodynamic properties of considered liquid alloys will be studied.**

- **The results obtained from molecular dynamics calculations will be compared with our earlier work.**

- **Thermodynamic, dynamic and surface properties calculations are done at 600K for Hg_1Pb_1 and at 298.15K for Hg_1In_1 resp.**

- **Structural and Transport properties are calculated at temperture for Hg_1Pb_1 at 623K and for Hg_1In_1 at 293K resp.**

7 Seminar/ Workshop/ Conference Attended

- ***Seminar cum workshop on First Principle and Other Simulation Methods in Condensed Matter Physics*** **held on 22-29 March 2010 in Himachal Pradesh University, Shimla.**
- ***56th DAE- Solid State Physics Symposium*** **held on 19-23 December 2011 at SRM University Kattangulattur, TamilNadu.**
- ***National Seminar on Experimental and Computational Techniques in Material Science*** **(ECTMS-2012) held on 31-2 April 2012 at Physics Department, Himachal Pradesh University, Shimla.**
- ***57th DAE- Solid State Physics Symposium*** **held on 3-7 December 2012 at Indian Institute of Technology Bombay.**

8 List of Publications

- **Anil Thakur, *Nalini Sharma*, P. K. Ahluwalia, Partial Structure Factors of Compound Forming Na-Pb Binary Liquid Alloy Using Ab-initio Pseudopotentials, AIP Conf. Proc. 1447 (2012)597.**
- ***Nalini Sharma*, Anil Thakur, P. K. Ahluwalia, Thermodynamical and Surface Properties of Compound Forming Liquid Amalgams (HgPb,HgIn), Physica B, (Communicated).**
- ***Nalini Sharma*, Anil Thakur, P. K. Ahluwalia, Electrical Resistivity of Compound Forming Liquid Amalgams (of Pb and In) Using Ab-initio Pseudopotentials, Physica B, (Communicated).**
- ***Nalini Sharma*, Anil Thakur, P. K. Ahluwalia, Structural and Electronic Transport Properties of Compound Forming $HgPb$ Liquid Alloy using Ab-initio Pseudopotential, 57th DAE- Solid State Physics Symposium held on 3-7 Dec. 2012 at IIT Bombay (Accepted).**
- **Anil Thakur, *Nalini Sharma*, Surjeet Chandel, P. K. Ahluwalia, Ab-initio Study of Liquid Systems: Concentration Dependence of Electrical Resistivity of Binary Liquid Alloy $Rb_{1-x}Cs_x$, 57th DAE- Solid State Physics Symposium held on 3-7 Dec. 2012 at IIT Bombay (Accepted).**

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